Molecule-based Magnets: Magnets for the 21st Century

by Joel S. Miller

The use and control of magnetism has enabled the ubiquitous availability of low-cost electricity and electric motors (large and small), as well as the development of telecommunications devices (telephones (terrestrial, cell, satellite), radios, televisions, etc.), and also information storage for computers, among a myriad of other equally important common uses. Furthermore, magnets are ideal components for sensors and actuators and are crucial for the development of smart materials/systems in the future. Classical magnets are composed of atoms of metals (transition or rare earth) or their ions, (*e. g.*, Fe, Co, CrO_2, $SmCo_5$, and $Nd_2Fe_{14}B$) and consequently have unpaired electron spins residing in *d*- or *f*-orbitals. The global 1999 production of magnetic materials is valued at $30 billion dollars with a projected growth of 10% per annum.[1] These magnets are fabricated by energy-intensive, high temperature metallurgical methods and are electrical conductors as well as being brittle. The latter half of the twentieth century has witnessed the replacement of many metal and ceramic materials with lightweight polymeric materials. This has been primarily for structural materials, but a growing number of examples are for electrically conducting and optical materials. Recently, new classes of magnetic materials based on molecules have been reported.[2] These new magnets are typically prepared at room temperature and benefit from organic syntheses methodologies that can lead to the controllable subtle modulation of the magnetic properties as well as the introduction of additional properties enabling the development of next generation magnetic and/or hybrid magnetic devices,[3] as has occurred in the areas of liquid crystals, electrically conducting polymers, and of course, in the pharmaceutical industry. A detailed history of magnets prepared from molecules, albeit an embryonic area, is available.4

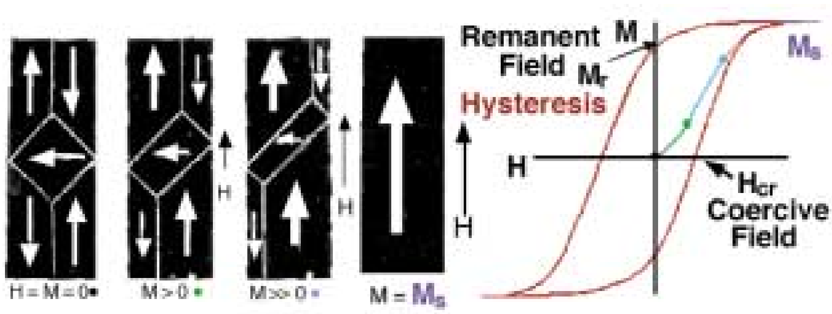

FIG. 1. Typical multidomain magnet and domain coalescing as a function of M(H) for an ordered ferro- or ferrimagnet exhibiting hysteresis.

The key property of a magnet is that, below a critical, magnetic ordering temperature, T_c, the magnetic moments for ferro- and ferrimagnets align in macroscopic small domains, which are still large on the molecular scale (Fig. 1, left hand side). While the direction of the magnetic moments of each domain differs, they can be aligned (via a minimal applied magnetic coercive field, H_{cr}), enhancing the net magnetization (M) up to a maximal value (the saturation magnetization, M_s), when all the spins throughout all domains align in the same direction. This leads to history dependent (hysteresis) magnetic behavior M(H) characteristic of ferri- and ferromagnets (Fig. 1). 'Soft' magnets have values of $H_{cr} < 10$ Oe and insignificant remanent magnetization, M_r; whereas 'hard' magnets have $H_{cr} > 100$ Oe and significant values of magnetization. Soft magnets are needed for ac motors and magnetic shielding, while hard magnets are necessary for the magnetic storage of data. The T_c, M_r, M_s, and H_{cr}, among others, are key parameters in ascertaining the commercial utility of a magnet. Magnetic materials that are subdomain in size are termed superparamagnetic; and they do not exhibit ordered behavior of extended magnets, unless a barrier exists to rotation of the spin of the superparamagnet. Many molecule-based magnets have values of T_c, M_r, M_s, and H_{cr} that are comparable to the commonly used magnetic materials.

Magnets made from molecules are a broad emerging class of new materials that extend the properties typically associated with magnets to include low-density, transparency, electrical insulation, low temperature fabrication, as well as combining magnetic ordering with other properties such as photo responses. Virtually all of the common magnetic properties associated with conventional metal and rare earth based magnets are also observed in molecule-based magnets. Molecule/organic-based magnets with magnetic ordering temperatures exceeding room temperature, very high (~27.0 kOe or 2.16 MA/m) and very low coercivities, as well as substantial remanent and saturation magnetizations, have been reported. In addition, exotic phenomena, including photomodulated magnetization, have been reported. Molecule-based magnets also offer new materials fabrication/processing opportunities as thin film magnets and can be prepared via low temperature (40°C) chemical vapor deposition and solution electrodeposition methods. This suggests that the next generation of electronic, magnetic, and/or photonic devices, ranging from magnetic imaging to data storage and to static and low frequency magnetic shielding and magnetic induction, may benefit from molecule-based magnetic materials. The latter application in static and low frequency magnetic shielding and magnetic induction is particularly promising, as relatively high initial permeabilities have been reported for the $V[TCNE]_x$.y (solvent) (TCNE = tetracyanoethylene) materials. This, combined with their low density (~1 g/cm^{-3}), rela-

(continued on page 46)

Molecule-based Magnets

(continued from page 21)

tively low resistivity (~10^4 ohm-cm), and low power loss suggest that future generations of these may be practical, especially for applications requiring low weight. Other potential applications include photocontrollable magnetism based on recent studies of Prussian blue-like, and $Mn[TCNE]_2$, materials.[5]

Thus, as Roald Hoffmann noted "Riches upon riches: reports of new discoveries, marvelous molecules, unmakeable, unthinkable yesterday - made today, reproducible with ease...incredible properties of novel high-temperature superconductors, organic ferromagnets..."[6] This issue of *Interface* focuses on the structure and magnetic properties of representative molecule-based magnets as studied in France, Japan, and in the United States.

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